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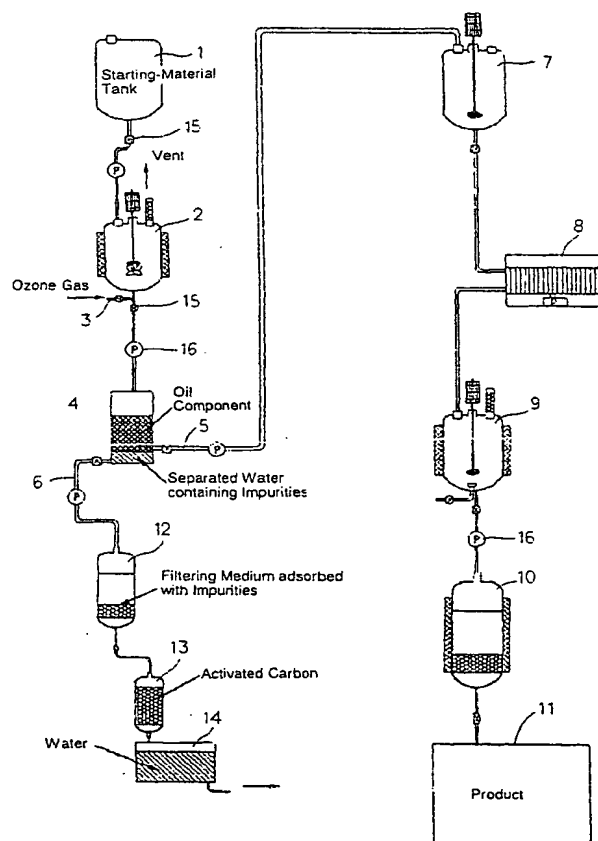
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ning of each regular issue of the PCT Gazette.

(54) Title: METHOD, APPARATUS AND PLANT FOR MANUFACTURING ENGINE FUEL



(57) Abstract: A method for manufacturing inexpensive and high-quality engine fuel, from a starting material comprising waste vegetable oils which have been conventionally wasted , is provided. There are provided; a starting-material tank (1) for storing oil/fat therein; a filtering device for filtering out solid components of the oil/fat in the starting-material tank; a first reaction vessel (5) for conducting first cracking by reacting ozone with the oil/fat; an oil/water separation device (4) for separating that water content involved in the cracking reaction, from the oil/fat; a first filtering device (8) for conducting first filtering of the oil/fat; a second reaction vessel (9) for conducting second cracking; a second filtering device (10); an adding device for adding an additive; an impurity adsorbing vessel (12) and a filtering vessel (13) for cooperatively purifying the water phase component from which the oil/fat phase has been excluded by the oil/water separation device; wherein in each of the first reaction and second reaction, there are delivered a reducing agent and polymerization inhibitor into the oil/fat.

DESCRIPTION

**METHOD, APPARATUS AND PLANT FOR MANUFACTURING
ENGINE FUEL**

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Technical Field

The present invention relates to a method, apparatus and plant for manufacturing engine fuels having lower boiling points from vegetable oils/fats having higher boiling points, and more particularly to a method, apparatus and plant for manufacturing engine fuels, adapted to exemplarily recycle used vegetable oils/fats having higher boiling points into diesel engine fuels having lower boiling points.

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Background Art

Reserves of fossil fuels or mineral oils such as petroleum, cork or natural gas buried in the earth are obviously limited, and are worried to be exhausted within several tens of years at the recent digging and consuming pace.

It has been officially reported that the annual amount of waste vegetable oils (waste cooking oils) in Japan is totally 400,000 tons including about 200,000 tons from companies such as food service industries and food processing factories and about 200,000 tons from general homes.

Relatedly, it has been confirmed that the annual amount of vegetable oils shipped from vegetable oil manufacturers is on the order of 1,000,000 to 1,500,000 tons, thereby suggesting that the amount of waste vegetable oils is actually more than reported. Today, the environmental pollution due to the waste vegetable oils (waste cooking oils) is closed up as a social problem to be solved immediately.

Concerning a part of waste vegetable oils, there has been recently known a so-called "methyl esterification technique" to be conducted in a process such as shown in FIG. 14. This technique is to recycle waste vegetable oils into diesel engine fuels, and adopts sodium hydroxide as a catalyst to thereby methyl-esterify a large amount of

simultaneously delivered methanol or ethanol.

However, the methyl esterification technique has the following problems. Namely, the production cost of fuels is high, because of the large amount of methanol or ethanol to be delivered into waste vegetable oils. The cost of plant construction becomes also high, in view of fire/accident prevention against the volatilities and lower flashing points of methanol and ethanol. Further, such characteristics of methanol and ethanol also cause a problem of job safety. Meantime, the fuels obtained in this manner tend to discharge combusted gases such as including large amounts of formaldehyde, acrolein, and benzene, thereby easily causing troubles on pistons, piston rings and in heads of engines.

As such, the present inventors of this invention have proposed and disclosed a method for purifying vegetable oils (virgin oils) or waste vegetable oils into diesel engine fuels (JP-A-2000-219886), to overcome the above defects of the methyl esterification technique.

According to the method and apparatus for purifying vegetable oils (virgin oils) or waste vegetable oils into diesel engine fuels proposed in the publication noted just above, it becomes possible to inexpensively purify waste vegetable oils into diesel engine fuels in a short time. Further, by virtue of no additional chemicals, the method leads to a reduced hazardousness to facilities and leads to substantially no waste products after purification, thereby simultaneously providing a remarkable effect as a recycling system. Moreover, the proposed fuels can be purifiedly obtained inexpensively by a simplified apparatus constitution in a short time, thereby allowing fully competing with commercially available fuels from a standpoint of cost. In addition, the proposed fuels have combustibility much superior to not only those fuels purified by the conventional methyl esterification technique but also commercially available light oils. Still more, upon adopting the proposed fuels in diesel engines, the amounts of CO₂, NO_x and SO_x in exhausted gases are as less as 50 % to 30 % of those conventional light oils, thereby meaning that the proposed ones are so clean as to remedy the atmospheric environment pollution.

It should have been epoch-making to obtain the method for purifying vegetable oils into diesel engine fuels by the above-proposed invention capable of

recycling waste vegetable oils into such excellent diesel engine fuels in an inexpensive manner substantially at ordinary temperatures.

Disclosure of Invention

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It is therefore an object of the present invention to provide a method, apparatus and plant for manufacturing engine fuel, which are capable of producing engine fuels of higher performances in addition to the aforementioned epoch-making ability.

To achieve the above object, the present inventors have discovered that,
10 adding a reducing agent and a polymerization inhibitor to the previously proposed purifying method for obtaining diesel engine fuels allows to more effectively and suitably adjust an oxidation cracking reaction to be caused by ozone, to thereby efficiently obtain engine fuels of a superior quality.

To this end, the present invention provides a method for manufacturing engine
15 fuel, comprising: a pretreatment step for filtering a higher-boiling-point vegetable oil/fat; a first treatment step for introducing ozone, a reducing agent and a polymerization inhibitor into the higher-boiling-point oil/fat, so as to cause the higher-boiling-point oil/fat component and the ozone to react with each other while adjusting the reactivity in the presence of the reducing agent and polymerization inhibitor, to
20 thereby crack the higher-boiling-point oil/fat component; a first filtering step for filtering the higher-boiling-point oil/fat so as to remove therefrom solid components including the reducing agent and polymerization inhibitor having been deteriorated by the cracking reaction; a second treatment step for newly introducing a fresh reducing agent and a fresh polymerization inhibitor both having higher activities and for
25 simultaneously introducing ozone, into the filtrate, so as to crack the higher-boiling-point oil/fat component while subsequently stirring the higher-boiling-point oil/fat component; and a step for repeating the treatment steps for cracking the higher-boiling-point oil/fat component in a manner to conduct such a treatment step totally two or more times while interposing the filtering step between the treatment steps, to
30 thereby reform the higher-boiling-point oil/fat into a lower-boiling-point oil while delivering an antifreeze agent into the lower-boiling-point oil.

It is preferable that the stirring treatments for breaking the constitution of the starting material to thereby cause a cracking phenomenon substantially require a stirring rotational speed of at least 10,000 rpm.

The vegetable oil may be a filtrate obtained by compressing waste vegetables.

5 It is preferable that the step for filtering out the solid components comprises a step for introducing and using a filtering medium including at least one of activated clay, diatomaceous earth, zeolite, activated carbon, and bone ash, at a rate of 20 kg to 25 kg for 1 kiloliter of the reaction liquid.

10 It is desirable that the treatment step comprises a step for introducing ozone in a form of ozone-containing air into the cracking reaction, at a concentration of 500 ppm to 30,000 ppm.

It is preferable that the reducing agent includes at least one of ferric oxide compound and copper compound, and is used at a rate of 0.15 g for 1 kiloliter of reaction liquid.

15 It is desirable that the polymerization inhibitor includes a phosphorus compound and is used at a rate of 0.2 g to 0.25 g for 1 kiloliter of reaction liquid.

It is preferable that the antifreeze agent includes castor oil and is introduced into the lower-boiling-point oil at a concentration of 0.05 wt.% to 0.1 wt.%.

20 The present invention provides a first apparatus for manufacturing engine fuel, which is an apparatus for manufacturing engine fuel by cracking a higher-boiling-point vegetable oil/fat to thereby reform the same into a lower-boiling-point oil, comprising: a reaction drum into which the higher-boiling-point oil/fat is introduced; and stirring means within the reaction drum; wherein the stirring means comprises: a rotating propeller plate for revolving a reaction liquid; and a baffle provided at an inner
25 periphery of the reaction drum; wherein the baffle comprises a vertical plate having a widthwise portion protruded from an inner peripheral wall surface of the reaction drum toward the center of the reaction drum, and the baffle is formed with saw-toothed cutouts at the protruded end; and wherein the reaction drum is provided with a delivering port for delivering a reducing agent and a polymerization inhibitor into the
30 reaction drum.

It is preferable that the rotating propeller plate comprises a propeller having a

peripheral portion formed with saw-toothed cutouts.

The present invention provides a second apparatus for manufacturing engine fuel, which is an apparatus for manufacturing engine fuel by cracking a higher-boiling-point vegetable oil/fat to thereby reform the same into a lower-boiling-point oil,

5 comprising: a reaction drum into which the higher-boiling-point oil/fat is introduced; stirring means within the reaction drum; an ozone gas introducing pipe having a spout for introducing ozone for causing a cracking reaction; and suspending means provided near the spout of the ozone gas introducing pipe, for suspending the ozone gas; wherein the suspending means is formed of a horizontal rotary-rod wound with wires
10 in a resilient manner; and wherein the reaction drum is provided with a delivering port for delivering a reducing agent and a polymerization inhibitor into the reaction drum.

The present invention further provides a plant for manufacturing engine fuel, comprising: a starting-material tank for storing oil/fat therein; a filtering device for filtering out solid components of the oil/fat in the starting-material tank; a first reaction
15 vessel for conducting first cracking by reacting ozone with the oil/fat filtered by the filtering device; an oil/water separation device for separating that water content involved in the cracking reaction, from the oil/fat; a filtering medium charging vessel for delivering a filtering medium into the oil/fat phase from which the water phase component has been excluded by the oil/water separation device; a first filtering
20 device for conducting first filtering of the oil/fat into which the filtering medium has been delivered; a second reaction vessel for reacting ozone with the filtered oil/fat, to thereby conduct second cracking; a second filtering device for conducting second filtering of the oil/fat subjected to the second cracking; an adding device for adding an additive into the oil/fat subjected to the second filtering; and an impurity adsorbing
25 vessel and a filtering vessel for cooperatively purifying the water phase component from which the oil/fat phase has been excluded by the oil/water separation device; wherein each of the first reaction vessel and the second reaction vessel is provided with a delivering port for delivering a reducing agent and a polymerization inhibitor into the reaction vessel.

30 Further objects, advantages and details of the present invention will become more apparent from the following description of preferred embodiments when read in

conjunction with the accompanying drawings.

Brief Description of Drawings

- 5 FIG. 1 is a schematic view of an embodiment of a manufacturing plant according to the present invention;
- FIG. 2 is a conceptional view of a first embodiment of a first reaction vessel;
- FIG. 3 is an enlarged view of a rotating propeller plate type stirring vane;
- FIG. 4 is a conceptional view of a second embodiment of the first reaction
- 10 vessel;
- FIG. 5 is a conceptional view of a natural separation type oil/water separating vessel;
- FIG. 6 is a conceptional view of a filtering medium charging vessel;
- FIG. 7 is a conceptional view of a first filtering device;
- 15 FIG. 8 is a conceptional view of a second reaction vessel;
- FIG. 9 is a conceptional view of a second filtering device;
- FIG. 10 is a conceptional view of a suction type filtering device;
- FIG. 11 is a conceptional view of a pressure type filtering device;
- FIG. 12 is a conceptional view of a product pretreatment device;
- 20 FIG. 13 is a schematic view of a manufacturing process; and
- FIG. 14 is a schematic view of a conventional methyl esterification process.

Best Mode for Carrying Out the Invention

- 25 There will be described hereinafter an embodiment of a method for manufacturing engine fuel according to the present invention.

<Manufacturing Method>

- 30 In manufacturing engine fuels, there are introduced ozone, a reducing agent and a polymerization inhibitor into a vegetable oil/fat having a higher boiling point. The vegetable oil/fat having the higher boiling point to be introduced with the

reducing agent and polymerization inhibitor includes at least one type such as selected from a group consisting of palm oil, palm nut oil, soybean oil, cotton seed oil, peanuts oil, sunflower oil, rape oil, corn oil, castor oil, olive oil, sesame oil, and linseed oil. These oils can be used solely or combinedly.

5 The vegetable oil/fat to be selected may be actually unused oils (virgin oils) and even used oils (waste oils) having already fulfilled inherent roles thereof. The filtrate obtained by compressing waste vegetables also will do, in any compressing scheme. Mixedly existing solid components shall be filtered out of oils/fats, by charging filtering mediums into the latter before filtration.

10 The filtering mediums to be used for filtering out solid components include activated clay, diatomaceous earth, zeolite, activated carbon, and bone ash. These mediums can be used solely or combinedly. The amount of filtering mediums to be used is preferably determined based on characteristics of the adopted filtering device.

15 Due to naturally higher boiling points and flashing points, the noted vegetable oils/fats can be never directly used as engine fuels nor readily discarded.

 In the embodiment of the present invention, ozone is introduced into a reaction liquid comprising a vegetable oil/fat having a higher boiling point, to thereby crack the oil/fat. The introduction of ozone can be conducted by ozone-containing air such as an ozone gas including air as a carrier gas, by ozone-containing water, or by a
20 combination thereof. The introduction of the ozone gas is conducted such as by bubbling from a bottom of liquid oil/fat.

 Together with ozone, the reducing agent is introduced into the vegetable oil/fat. Such a reducing agent to be introduced together with ozone includes ferric oxide, and copper compounds.

25 The polymerization inhibitor is introduced together with the reducing agent. Such a polymerization inhibitor to be introduced together with the reducing agent includes phosphorus compounds.

 In case of the ozone-containing air including air as the carrier gas, the concentration of ozone to be introduced into the reaction liquid is desirably 500 ppm to
30 30,000 ppm, and preferably 2,000 ppm to 10,000 ppm, such as in terms of a state under a standard pressure.

In case of the ozone-containing water, there is exemplarily introduced saturated water. Desirably, the introduction ratio is exemplarily 3 wt.% to 8 wt.% of the whole reaction liquid inclusive of the introduced ozone-containing water.

The ratio of the reducing agent to be introduced together with ozone is
5 desirably on the order of 0.15 g at one time for 1 kiloliter of reaction oil/fat per one step. In case of repeated steps of two or more times, newly introduced for each of repeated steps is 0.15 g of the reducing agent for 1 kiloliter of reaction oil/fat.

The ratio of the polymerization inhibitor to be introduced together with the reducing agent is desirably 0.2 g to 0.25 g for 1 kiloliter of reaction oil/fat, for example.
10 In case of repeated steps of two or more times, newly introduced for each of repeated steps is 0.2 g to 0.25 g of the polymerization inhibitor for 1 kiloliter of reaction oil/fat.

Cracking reactions of oils/fats are typically conducted by supplying ozone thereto, under rotational stir. Supply of the ozone gas is conducted, while bubbling an ozone-containing gas into the reaction liquid.

15 The cracking reaction is conducted while vigorously revolving the reaction liquid. This is preferably conducted by adopting a stirrer having a higher shearing effect. In case of adopting a stirring device having a lower shearing effect, the stirring speed might be suitably 10,000 rpm to 30,000 rpm, for example. In case of adopting a stirrer having a higher shearing effect, 250 rpm to 1,000 rpm, and even 350 rpm to 500
20 rpm will do sometimes. Higher rotational rates are not desirable from the viewpoint of job safety management. In that meaning, it is greatly advantageous to adopt a stirrer having a higher shearing effect.

The reaction temperature is to be lower than the flashing point and ignition point of the reaction oil/fat, and desirably 40 °C to 80 °C, for example. In case of
25 cracking a fatty material which is solid at ordinary temperatures, the cracking is conducted at temperatures higher than the fluidizing temperature of the material. In case of introducing ozone in the form of ozone water, it is preferable to introduce the ozone water having been previously adjusted to the reaction temperature. The reaction time may be roughly 0.5 to 2 hours.

30 Conducting such a cracking reaction allows reforming an oil/fat having a higher boiling point into one having a lower boiling point. It is possible to decide the

termination of the cracking reaction based on the value of the boiling point.

After the reaction has terminated, it is generally preferable to remove the reducing agent and polymerization inhibitor having been provided for the reaction. The removal is exemplarily conducted by filtration. Filtering mediums to be used for the filtration include activated clay, diatomaceous earth, zeolite, activated carbon, and bone ash. These mediums can be used solely or combinedly.

It is preferable to introduce the filtering medium at the rate of 20 kg to 25 kg to 1 kiloliter of reaction liquid. The filtering operation is preferably conducted in a usual manner. The filtration is preferably conducted at temperatures lower than the flashing point and higher than 65 °C.

In case of introducing ozone in the form of ozone-containing water into the reaction liquid, the reaction liquid after termination of the reaction is subjected to oil/water separation, thereby separating water phase components. In this way, those water-soluble impurities, which might deteriorate the performance as engine fuel, dissolve in water and are excluded from the lower-boiling-point oil.

The filtrate after termination of the cracking reaction includes those variously mixed oily substances having lower boiling points, which have been obtained by cleaving oils/fats at sites of unsaturated groups thereof. When the boiling points of the oily substances are substantially equivalent to those of kerosene and light oil, the substances can be preferably used as diesel engine fuels.

It is generally preferable that the lower-boiling-point oil obtained by the cracking reaction is mixed with an antifreeze agent before or after the reaction. The antifreeze agent may exemplarily include castor oil. The antifreeze agent is preferably mixed into the lower-boiling-point oil at a ratio of 0.05 wt.% to 0.1 wt.%.

The thus obtained lower-boiling-point oil may be further mixed with required additives.

<Manufacturing Plant>

Manufacturing of engine fuels from vegetable oils/fats is preferably conducted throughout multiple steps such as by utilizing a manufacturing plant to be described hereinafter.

FIG. 1 is a schematic view of an embodiment of the manufacturing plant according to the present invention.

There are provided a starting-material tank 1 for storing vegetable oils/fats therein, and a first reaction vessel 2 downstream of the starting-material tank 1.

5 Extended from a bottom of the first reaction vessel 2 is an outlet pipe merged with an ozone gas tube 3.

Provided downstream of the first reaction vessel 2 is an oil/water separation vessel 4. Extended from the oil/water separation vessel 4 are an oil phase pipe 5 and an aqueous phase pipe 6. There are provided a filtering medium charging vessel 7
10 downstream of the oil phase pipe 5 of the oil/water separation vessel 4, a first filtering device 8 downstream of the filtering medium charging vessel 7, and a second reaction vessel 9 downstream of the first filtering device 8. Further, there are provided a second filtering device 10 downstream of the second reaction vessel 9, and a product storage tank 11 downstream of the former.

15 Provided downstream of the aqueous phase pipe 6 of the oil/water separation vessel 4 are an impurity adsorbing vessel 12 filled with an impurity adsorbent, and a filtering vessel 13 downstream of the impurity adsorbing vessel 12 and filled with activated carbon, followed by an ozone injecting vessel 14.

Provided at appropriate locations are automatic circulation controlling valves
20 15 and pumps 16, so as to duly block the circulation.

FIG. 2 is a conceptional view of a first embodiment of the first reaction vessel 2. This vessel comprises a hollow drum body 21 having its peripheral wall mounted therearound with a heater jacket 22. The upper portion of the drum body is communicated with the oil phase pipe extended from the starting-material tank 1, and
25 is provided with a reducing agent/polymerization inhibitor delivering port 23. Mounted within the drum body 21 are vertically extended baffles 24 in a manner to protrude widthwise portions of the baffles 24 toward the center of the drum body, respectively, and the baffles 24 are provided with saw-toothed cutouts at the protruded ends, respectively.

30 Vertically inserted into the central portion of the drum body 21 is a stirring rod 26 interlocked with a stirring motor 25. The stirring rod 26 is provided with, at a

plurality of portions of its middle part and at its lower end, stirring vanes 27 and a stirring vane 28 which is formed of a rotating propeller plate, respectively, to thereby constitute a stirrer.

Extended from the lower portion of the drum body 21 is a composite
5 discharging pipe. Closest to the connecting port of the drum body 21, this composite discharging pipe is merged with a tip end of the ozone gas tube 3 communicating with an ozone generator, so as to allow the ozone gas to flow backward through the near-root portion of the discharging pipe to thereby enter the drum body 21. The upper
10 portion of the drum body 21 is provided with a gas vent 29 loaded with an activated carbon cylinder.

FIG. 3 is an enlarged view of the rotating propeller plate type stirring vane 28. This rotating propeller plate type stirring vane 28 at the lower end of the stirring rod is provided with saw-toothed cutouts at its periphery. The stirring vane 28 may include
15 three vanes 28(a) or four vanes 28(b) as shown in FIG. 3. The rotating propeller plate type stirring vane 28 integrally cooperates with the baffles 24 to thereby exhibit a shearing effect to the reaction liquid.

FIG. 4 is a conceptional view of a second embodiment of the first reaction vessel 2. Adopted at the lower end of the stirring rod 26 is a stirring vane 27 of the same type as that at the middle part of the stirring rod, instead of the rotating propeller
20 plate type.

Further, penetrated through the lower interior of the first reaction vessel 2 is a horizontal rotary-rod 30, which has a central rotating axis extending in the longitudinal direction of the rod itself and which can be rotated by a rotary motor 31. The horizontal rotary-rod 30 is wound with wires in a resilient wire-brush shape, in a
25 region inserted within the drum body. The remaining parts are the same as the first embodiment shown in FIG. 2.

FIG. 5 is a conceptional view of the natural separation type oil/water separation vessel 4 provided downstream of the first reaction vessel 2. The interior of the vessel is divided into an upper aqueous phase region and a lower oil phase region.
30 Extended from the oil phase region and aqueous phase region are the oil phase pipe 5 and aqueous phase pipe 6, respectively. The oil/water separation vessel 4 is not

necessarily limited to the natural separation type, and it is possible to alternatively and exemplarily adopt an oil/water centrifuge.

FIG. 6 is a conceptional view of the filtering medium charging vessel 7 communicated with the oil phase pipe 5 extended from the oil/water separation vessel 4. This vessel comprises a hollow drum body having an upper portion communicated with the oil phase pipe 5 extended from the oil/water separation vessel 4. The drum body is internally provided with a stirrer 42.

FIG. 7 is a conceptional view of the first filtering device 8 downstream of the filtering medium charging vessel 7. The first filtering device 8 is provided with parallelly arranged multiple filtering plates 43, and has a built-in pressurizing pump 44.

FIG. 8 is a conceptional view of the second reaction vessel 9. This is substantially similar to the first embodiment of the first reaction vessel 2. However, no baffles are provided, and the stirring vane 28 is provided at the lowermost end of the stirring rod 26. Provided at the lower interior of the drum body is babble suspending means 45 for suspending ozone babbles within the liquid phase. Mounted at the upper portion of the drum body is the gas vent 29 loaded with an activated carbon cylinder.

As the second reaction vessel 9 to be provided downstream of the first filtering device 8, it is possible to adopt the same type of reaction vessel as the first reaction vessel 2 illustrated in FIG. 2 or FIG. 4.

FIG. 9 is a conceptional view of the second filtering device 10 to be provided downstream of the second reaction vessel 9. This vessel comprises a hollow drum body having its peripheral wall mounted therearound with the heater jacket 22, and the lower portion of the drum body is filled with a filtering medium 46. The upper portion of the drum body is provided with an inlet connected with the composite discharging pipe extended from the second reaction vessel 9. Extended from the interior lowermost portion of the drum body is a filtrate discharging pipe communicated to the product storage tank 11.

Note, it is generally preferable to provide a pretreatment filtering device on the communicating path from the starting-material tank 1 toward the first reaction vessel 2, unlike the embodiment shown in FIG. 1. Such a filtering device may be of a pressure type or suction type.

FIG. 10 is a conceptional view of a filtering device 50 of the noted suction type. This device comprises two drum bodies 51, 52 vertically stacked in a two-staged manner, and the upper portion of the upper drum body 51 is communicated with the discharging pipe of the starting-material tank 1. There is also provided a flowing pipe
5 emerging from the lower portion of the drum body 51 and entering the upper portion of the lower drum body. Provided within the drum body 51 is a horizontal receiving plate formed with many punched through-holes, and the horizontal receiving plate carries thereon an accumulated filtering medium 51a. The lower drum body 52 is adapted to be sucked by a vacuum pump 53, while allowing a discharging pipe to
10 extend from the lower portion of the lower drum body 52 toward the first reaction vessel 2.

FIG. 11 is a conceptional view of a suction type filtering device 50 of the noted pressure type. This device is provided with mutually and in parallel arranged filtering plates 43, and with a plate 54 for disposing of used filtering mediums. The
15 pressurizing pump 44 is also provided externally.

Those filtering devices of the same types as those illustrated in FIG. 10 and FIG. 11 can be of course utilized as the first filtering device 8 and second filtering device 10 provided downstream of the filtering medium charging vessel 7 and second reaction vessel 9, respectively.

20 It may be rather preferable to render the filtrate discharging pipe from the second filtering device 10 toward the product storage tank 11 to midway pass through a product pretreatment device, unlike the embodiment shown in FIG. 1 where such a pipe is directly extended to the product storage tank 11.

FIG. 12 is a conceptional view of a product pretreatment device 60. This
25 device comprises a hollow drum body internally provided with a stirrer having a motor, and the upper portion of the drum body is communicated to the filtrate discharging pipe from the second filtering device 10. Provided at the upper portion of the drum body is an additive delivering port 61 having an additive measuring device, while allowing a discharging pipe extended from the lower portion of the drum body to
30 communicate with the product storage tank 11.

<Manufacturing in Plant>

In manufacturing engine fuels, the aforementioned manufacturing plant is exemplarily used to conduct the following steps.

FIG. 13 is a flowchart schematically showing a manufacturing process. To
5 exemplarily manufacture engine fuels from waste vegetable oils as shown in FIG. 13, it is typical to conduct a pretreatment step, first treatment step, first filtering step, second treatment step, second filtering step, and other additional steps.

The pretreatment step is to remove solid components mixedly existing in the oil/fat.

10 The first treatment step is to crack the oil/fat contents having been left by removing solid components therefrom.

The first filtering step includes an oil/water separating step for removing the water content having been added due to the first cracking step, and a step for removing impurities mixedly existing in the oil phase separated from the water content.

15 The second treatment step is to crack the oil/fat contents again.

The second filtering step includes a step for removing impurities mixedly existing within the oil phase.

The other additional steps comprise an impurity removing step and a refluxing step. The impurity removing step is to remove mixed components other than water
20 content from the aqueous phase separated by the oil/water separation, to thereby purify the aqueous phase. The refluxing step is to inject ozone into the purified water, and to reflux the ozone-injected water to the first cracking step.

The aforementioned steps are exemplarily performed in the following manner such as by utilizing the aforementioned manufacturing plant.

25 The starting-material tank 1 is introduced with vegetable oil/fat. When solid components are mixedly existing in the oil/fat, the pretreatment step is conducted. Namely, the oil/fat is fed to the first treatment step via pretreatment filtering device 60. In case of a lot of solid components mixedly existing in the oil/fat, it is desirable to mix filtering mediums into the oil/fat at the stage of the starting-material tank 1, and
30 thereafter to render the oil/fat to pass through the pretreatment filtering device. Particularly, in utilizing the pressure type filtering device 50 (filter press) including

arranged in parallel multiple filtering plates 43, filtering mediums acting as a flocculant are mixed into the oil/fat before introducing it into the filtering device 50.

The oil/fat having passed through the pretreatment step is introduced into the first treatment step, i.e., into the first reaction vessel 2. The first reaction vessel 2 is also delivered with a reducing agent/polymerization inhibitor. It is suitable to add ozone water dissolved with ozone into the oil/fat.

The interior of the first reaction vessel 2 is adjusted to a reaction temperature range for the cracking reaction. Ozone gas is introduced into the vessel from the ozone gas tube 3. The ozone gas is backwardly flowed through the root portion of the discharging pipe of the first reaction vessel 2 into the drum body of this vessel, to thereby cause babbling within the first reaction vessel 2. The interior of the first reaction vessel 2 is stirred by the stirrer. In this way, the oil/fat is applied with the first cracking reaction treatment.

The oil/fat having finished the first cracking reaction treatment is introduced into the first filtering step. The oil/water separation vessel 4 firstly conducts oil/water separation. The oil phase portion is transferred to the filtering medium charging vessel 7 where filtering mediums are delivered thereinto. The oil/fat delivered with filtering mediums is then filtered by the first filtering device 8.

In the second treatment step, there is conducted a second cracking reaction in the second reaction vessel 9. The second cracking reaction treatment is substantially the same as the first cracking reaction treatment. Upon termination of the second cracking reaction, it is possible to deliver an antifreeze agent into the oil/fat at that time.

The oil/fat is then introduced into the second filtering step. Namely, the oil/fat is filtered by the second filtering device 10. Then, the oil/fat is mixed with required additives and thereafter transferred to the product storage tank 11.

The aqueous phase obtained at the oil/water separation vessel 4 by the oil/water separation is treated by the other additional steps. Namely, the aqueous phase is purified via impurity adsorbing vessel 12 and filtering vessel 13, and is injected with ozone at the ozone injecting vessel 14. The thus ozone-injected water is refluxed to the first reaction vessel 2.

<Features>

The manufacturing method utilizing the aforementioned plant and apparatus exhibit the following features.

5 The pertinent oil/fat is passed through the pretreatment filtering device in the pretreatment step, thereby allowing to recycle such oils/fats of relatively low quality containing solid impurities.

According to the first reaction vessel 2 utilizing the baffles and rotating propeller plate type stirring vane 28, it becomes possible to apply a relatively large shearing load to the reaction liquid even by a smaller rotational rate thereof. This
10 allows to subject chain molecules of higher molecular weights to a cleavage reaction (cracking reaction), even without subjecting the reaction liquid to high-speed rotational loads likely to cause dangerousness.

The stirring rod is mounted with the multiple stirring vanes, so that various components contained in the reaction liquid can be substantially homogenized in terms
15 of concentrations.

Within the first reaction vessel 2 inserted with the horizontal rotary-rod wound with wires in a resilient wire-brush shape, bubble diameters of the ozone gas in the reaction liquid are reduced to thereby increase surface areas of gas/liquid contacting interfaces, thereby allowing to efficiently progress the reaction.

20 The first reaction vessel 2 utilizes ozone water. Introduction of the ozone water into the reaction liquid allows water-soluble components in the pertinent oil/fat to be extracted into the thus introduced aqueous phase.

Ozone tends to dissolve in oil rather than in water. Adopting ozone water allows supplying a large amount of ozone into the oily reaction liquid. Ozone has a
25 higher oxidizability, and oxidizes various substances. Those substances turned to be water-soluble by oxidization are extracted into the aqueous phase.

At each of the first reaction vessel 2 and second reaction vessel 9, there are delivered a reducing agent and a polymerization inhibitor. This allows to adjust the oxidation reaction caused by ozone to thereby avoid such a situation that the cracking
30 reaction is excessively progressed to result in oils/fats of excessively lower boiling points or that the oils/fats are polymerized into oils/fats of higher boiling points.

Namely, ozonides are effectively inverted into aldehydes and ketones, to thereby efficiently produce engine fuels of high quality.

Those ozone molecules, which are not involved in the reaction and thus depart from the reaction liquid, remain within the first reaction vessel 2 or second reaction vessel 9. However, these ozone molecules are no way diffused into the atmosphere, because the gas vent 29 is mounted with the activated carbon cylinder.

Those components extracted into the aqueous phase are separated from the water, through the impurity adsorbing vessel 12 and filtering vessel 13. Those components separated from the water can be mixed into compost and combinedly recycled as fertilizer.

The oil/fat contents are cleaved by the cracking reaction to be conducted two times. Even the oil/fat passed through the first filtering step typically has a sufficient combustion performance as fuel. Nonetheless, repeating the cracking reaction twice allows further improving the performance.

Higher-boiling-point oils/fats are cleaved at sites of unsaturated groups thereof, and reformed into substances having boiling points like light oils. Adopting vegetable oils/fats allows to exhibit sufficient capabilities as diesel engine oil, and to occasionally expect a function exceeding even mineral-oil-derived light oil. Further, vegetable oils are cleaved at sites of predetermined unsaturated groups, so that boiling points are never excessively lowered. Upon manufacturing, those substances having lower flashing points such as ethyl alcohol and methyl alcohol are never involved, thereby attaining higher job safety.

Adding the antifreeze agent allows to obtain reformed oils/fats of high performance which can be durably used even in winter.

Since the ozone water for supplying ozone is refluxed, it is enough to supplement that amount of ozone which has been involved in the cracking reaction, to thereby substantially improve the reaction efficiency of ozone.

The first reaction vessel 2 and second reaction vessel 9 are provided with gas vents 29 at the upper portions of the drum bodies 21, respectively, and the gas vents 29 are mounted with activated carbon cylinders, respectively, thereby preventing ozone having a strong oxidizability from directly diffusing into the atmosphere.

[Embodiment]

There will be explained hereinafter an embodiment of the present invention.

There was assembled a model of the plant shown in FIG. 1, so as to reform waste tempura oil in the following method. The suction type filtering device 50 was added as the pretreatment step, while adopting the first embodiment of the first reaction vessel 2. Further, the oil was passed through the product pretreatment device 60, before storing the oil into the product storage tank 11.

Waste tempura oil was introduced into the starting-material tank 1, and then transferred into the filtering device 50 so as to remove mixedly existing solid components. The filtering device 50 was filled with activated clay as filtering medium.

The waste oil filtered by the activated clay was transferred into the first reaction vessel 2, and subjected to first cracking for 60 minutes after delivering a reducing agent and polymerization inhibitor into the waste oil.

Ozone was introduced by means of ozone water delivered before starting the reaction, and additionally introduced by means of ozone gas. Stirring was conducted by revolving the reaction liquid at 500 rpm.

The oil/fat subjected to the first cracking was separated into an oil phase and an aqueous phase by the oil/water separation vessel 4, and the oil phase was introduced into the filtering medium charging vessel 7. The filtering medium charging vessel 7 was further delivered with activated clay, and then the first filtering was conducted.

The oil/fat subjected to the first filtering was transferred to the second treatment step. There was conducted the second cracking step in the second reaction vessel 9. Ozone was supplied by means of ozone gas. The ozone gas including air as carrier gas was continuously supplied for 1 hour at an ozone concentration of 2,000 ppm. Stirring of the reaction liquid was conducted by revolving the reaction liquid at a rate of 2,000 rpm. Ferric oxide and polymerization inhibitor were delivered into the reaction liquid. The reaction time was 1 hour.

Castor oil as an antifreeze agent was delivered into the reaction liquid.

Then, the reaction liquid was filtered by the second filtering device 10, while adopting activated clay as filtering medium. Upon termination of the second filtering

step, the filtrate was transferred to a step for adding additives into the filtrate.

Meanwhile, the aqueous phase separated from the oil phase by the oil/water separation vessel 4 was purified by passing through the impurity adsorbing vessel 12 and filtering vessel 13, and the thus purified water was injected with ozone at the
5 ozone injecting vessel 14 so as to be prepared for the next operation.

The thus obtained lower-boiling-point oils were analyzed, and the result thereof is shown in Table 1.

Table 1

	Unit	Light oil (Idemitsu)	Methyl-esterification Domestic standard	Methyl-esterification EU standard	Methyl-esterification Domestic company	Revive fuel (vegetable) (Embodiment)
Density 15°C	g/cm ³	0.835	0.86 to 0.90	0.86 to 0.90	0.8828	0.8758
Flash point	°C	65	Min 100	Min 100	130.1	51.3
Clogging point	°C	-8	Max-5	Max-15	-6	-37
Total exotherm	Kcal/kg	10,920	9,500	9,500	9,490	9,730
Distillation test Initial boiling point	°C	170	Not designated	Not designated	185	161.5
10% °C	°C	220	Not designated	Not designated	320	181.5
50% °C	°C	280	Not designated	Not designated	337	216
Terminal point °C	°C	360	Not designated	Not designated	362	342
Sulfur content	%	0.2 or less	Max 0.01	Max 0.01	0.01	0.01

10 The above result has clarified that the obtained lower-boiling-point oils ("Revive fuel") have higher purity and more excellent properties than: the domestic standard for methyl esterification in Japan; and even the standard for methyl esterification in EU. Particularly, the performance excellence of the obtained oils can be seen, as compared with the relevant and listed fuel which is purifiedly provided by

a certain company in Japan. In this respect, it is important to note the resultant values of the distillation tests, in terms of analyses of fuels. Namely, in the distillation tests of Table 1, the revive fuel has excellent values even than the light oil manufactured by Idemitsu Kosan Co., Ltd., in Japan. This fact clearly shows how fine the liquid particles in the revive fuel are minimized. In this way, minimizing particle diameters of fuel to be injected into an internal combustion engine allows avoiding incomplete combustion in the engine and rather allows complete combustion. Such complete combustion renders the exhausted gas to be free of harmful substances while generating no graphites. This permits to expect remedies for the recent social problem of environmental pollution due to exhausted gases from diesel engines.

Industrial Applicability

As described above, the method, apparatus and plant for manufacturing engine fuel of the present invention are provided to reform vegetable oils/fats of higher boiling points into lower-boiling-point oils, and involve higher safety concerning fire/accident prevention by virtue of exclusion of highly flammable substances such as methyl alcohol and ethyl alcohol.

The higher safety concerning fire/accident prevention allows to inexpensively assemble the manufacturing apparatus and construct the manufacturing plant, thereby inexpensively manufacturing engine fuels.

Moreover, adopting the reducing agent and polymerization inhibitor allows to adjust the oxidation reaction caused by ozone to thereby avoid such a situation that the cracking reaction is excessively progressed to result in oils/fats of excessively lower boiling points or that the oils/fats are polymerized into oils/fats of higher boiling points. This permits to realize manufacturing of excellent diesel engine fuels from waste vegetable oils as starting materials which have been conventionally wasted.

CLAIMS

1. A method for manufacturing engine fuel, comprising:

a pretreatment step for filtering a higher-boiling-point vegetable oil/fat;

5 a first treatment step for introducing ozone, a reducing agent and a polymerization inhibitor into the higher-boiling-point oil/fat, so as to cause the higher-boiling-point oil/fat component and the ozone to react with each other while adjusting the reactivity in the presence of the reducing agent and polymerization inhibitor, to thereby crack the higher-boiling-point oil/fat component;

10 a first filtering step for filtering the higher-boiling-point oil/fat so as to remove therefrom solid components including the reducing agent and polymerization inhibitor having been deteriorated by the cracking reaction;

a second treatment step for newly introducing a fresh reducing agent and a fresh polymerization inhibitor both having higher activities and for simultaneously
15 introducing ozone, into the filtrate, so as to crack the higher-boiling-point oil/fat component while subsequently stirring the higher-boiling-point oil/fat component; and

a step for repeating said treatment steps for cracking the higher-boiling-point oil/fat component in a manner to conduct such a treatment step totally two or more times while interposing said filtering step between said treatment steps, to thereby
20 reform the higher-boiling-point oil/fat into a lower-boiling-point oil while delivering an antifreezing agent into the lower-boiling-point oil.

2. A method for manufacturing engine fuel of claim 1,

wherein said stirring treatments for breaking the constitution of the starting
25 material to thereby cause a cracking phenomenon substantially require a stirring rotational speed of at least 10,000 rpm.

3. A method for manufacturing engine fuel of any one of claims 1 and 2,

wherein the vegetable oil is a filtrate obtained by compressing waste
30 vegetables.

4. A method for manufacturing engine fuel of any one of claims 1 through 3,

wherein said step for filtering out the solid components comprises a step for introducing and using a filtering medium including at least one of activated clay, diatomaceous earth, zeolite, activated carbon, and bone ash, at a rate of 20 kg to 25 kg to 1 kiloliter of the reaction liquid.

5

5. A method for manufacturing engine fuel of any one of claims 1 through 4, wherein said treatment step comprises a step for introducing ozone in a form of ozone-containing air into the cracking reaction, at a concentration of 500 ppm to 30,000 ppm.

10

6. A method for manufacturing engine fuel of any one of claims 1 through 5, wherein the reducing agent includes at least one of ferric oxide compound and copper compound, and is used at a rate of 0.15 g for 1 kiloliter of reaction liquid.

15

7. A method for manufacturing engine fuel of any one of claims 1 through 6, wherein the polymerization inhibitor includes a phosphorus compound and is used at a rate of 0.2 g to 0.25 g for 1 kiloliter of reaction liquid.

20

8. A method for manufacturing engine fuel of any one of claims 1 through 7, wherein the antifreezing agent includes castor oil and is introduced into the lower-boiling-point oil at a concentration of 0.05 wt.% to 0.1 wt.%.

25

9. An apparatus for manufacturing engine fuel by cracking a higher-boiling-point vegetable oil/fat to thereby reform the same into a lower-boiling-point oil, comprising:

a reaction drum into which the higher-boiling-point oil/fat is introduced; and stirring means within said reaction drum;

wherein said stirring means comprises: a rotating propeller plate for revolving a reaction liquid; and a baffle provided at an inner periphery of said reaction drum;

30

wherein said baffle comprises a vertical plate having a widthwise portion protruded from an inner peripheral wall surface of said reaction drum toward the

center of said reaction drum, and said baffle is formed with saw-toothed cutouts at the protruded end; and

wherein said reaction drum is provided with a delivering port for delivering a reducing agent and a polymerization inhibitor into said reaction drum.

5

10. An apparatus for manufacturing engine fuel of claim 9,
wherein said rotating propeller plate comprises a propeller having a peripheral portion formed with saw-toothed cutouts.

10

11. An apparatus for manufacturing engine fuel by cracking a higher-boiling-point vegetable oil/fat to thereby reform the same into a lower-boiling-point oil, comprising:

a reaction drum into which the higher-boiling-point oil/fat is introduced;

stirring means within said reaction drum;

15

an ozone gas introducing pipe having a spout for introducing ozone for causing a cracking reaction; and

suspending means provided near said spout of said ozone gas introducing pipe, for suspending the ozone gas;

20

wherein said suspending means is formed of a horizontal rotary-rod wound with wires in a resilient manner; and

wherein said reaction drum is provided with a delivering port for delivering a reducing agent and a polymerization inhibitor into said reaction drum.

25

12. A plant for manufacturing engine fuel, comprising:

a starting-material tank for storing oil/fat therein;

a filtering device for filtering out solid components of the oil/fat in said starting-material tank;

a first reaction vessel for conducting first cracking by reacting ozone with the oil/fat filtered by said filtering device;

30

an oil/water separation device for separating that water content involved in the cracking reaction, from the oil/fat;

a filtering medium charging vessel for delivering a filtering medium into the oil/fat phase from which the water phase component has been excluded by said oil/water separation device;

5 a first filtering device for conducting first filtering of the oil/fat into which the filtering medium has been delivered;

a second reaction vessel for reacting ozone with the filtered oil/fat, to thereby conduct second cracking;

a second filtering device for conducting second filtering of the oil/fat subjected to the second cracking;

10 an adding device for adding an additive into the oil/fat subjected to the second filtering; and

an impurity adsorbing vessel and a filtering vessel for cooperatively purifying the water phase component from which the oil/fat phase has been excluded by said oil/water separation device;

15 wherein each of said first reaction vessel and said second reaction vessel is provided with a delivering port for delivering a reducing agent and a polymerization inhibitor into said reaction vessel.

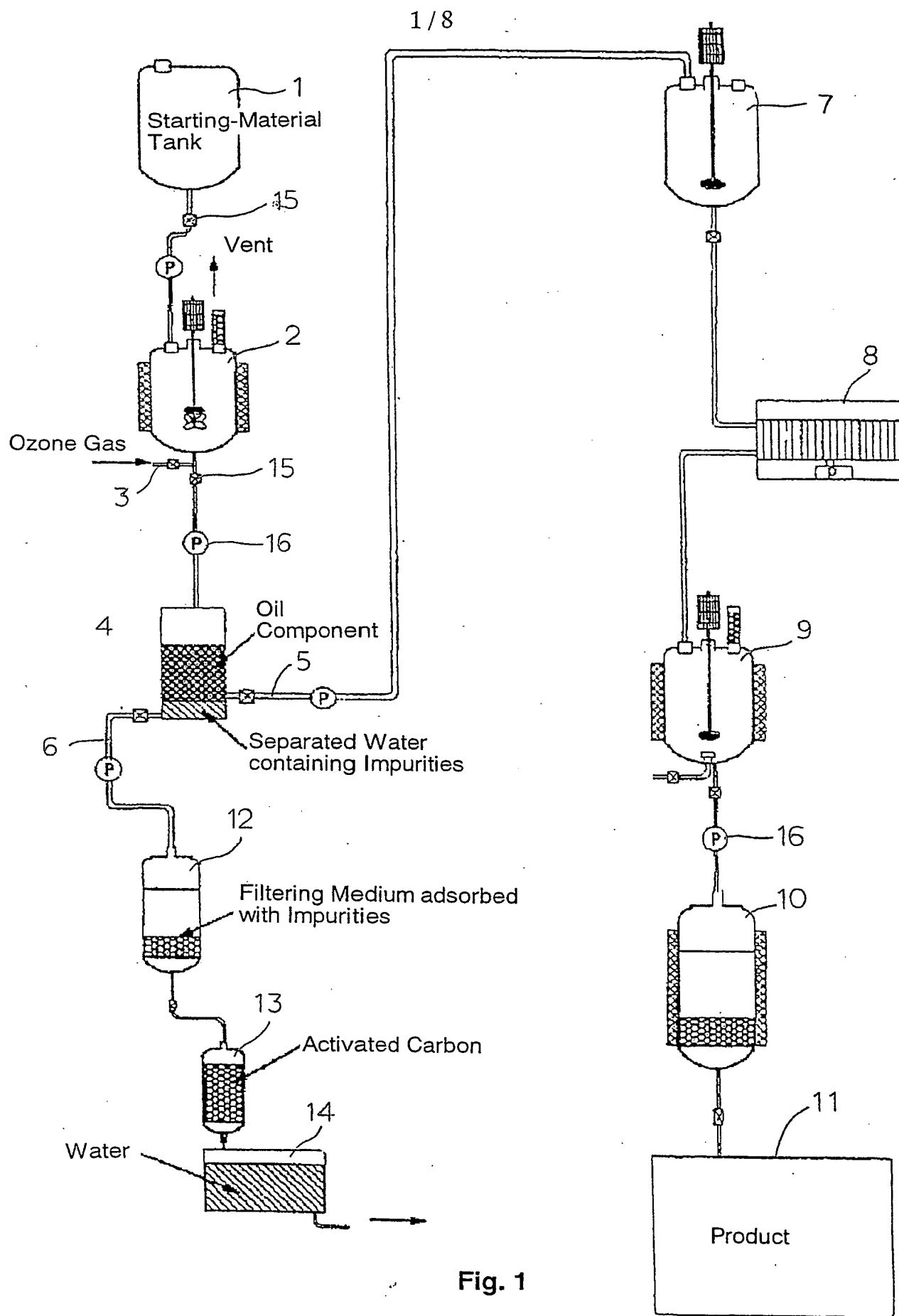
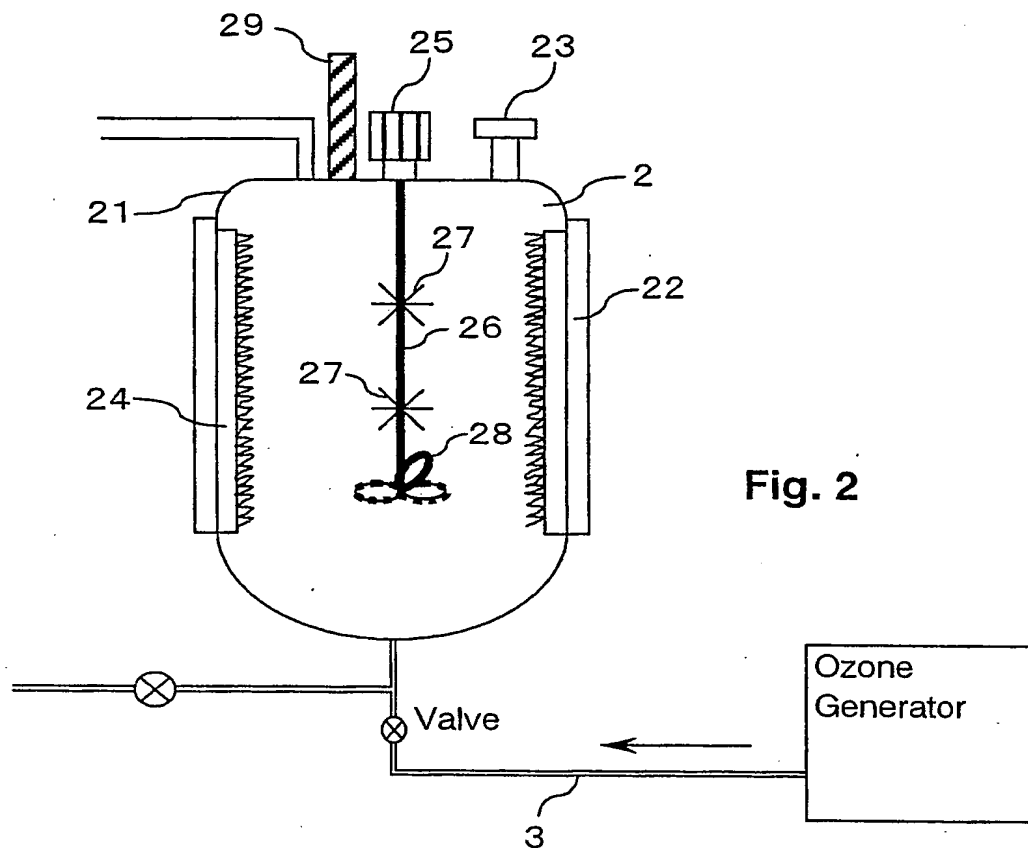


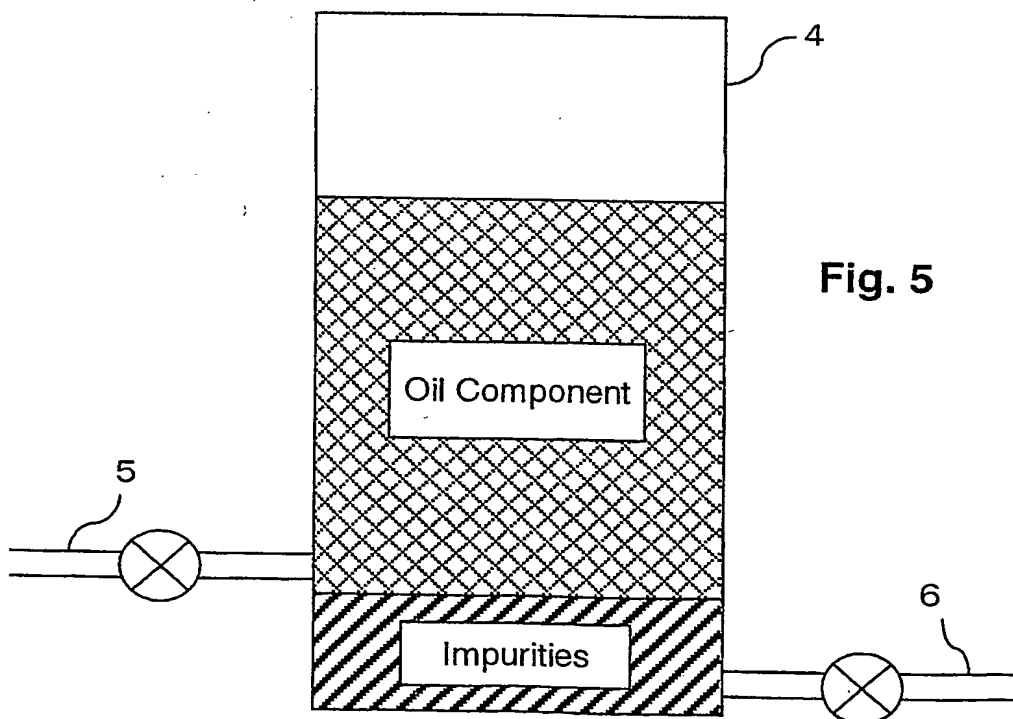
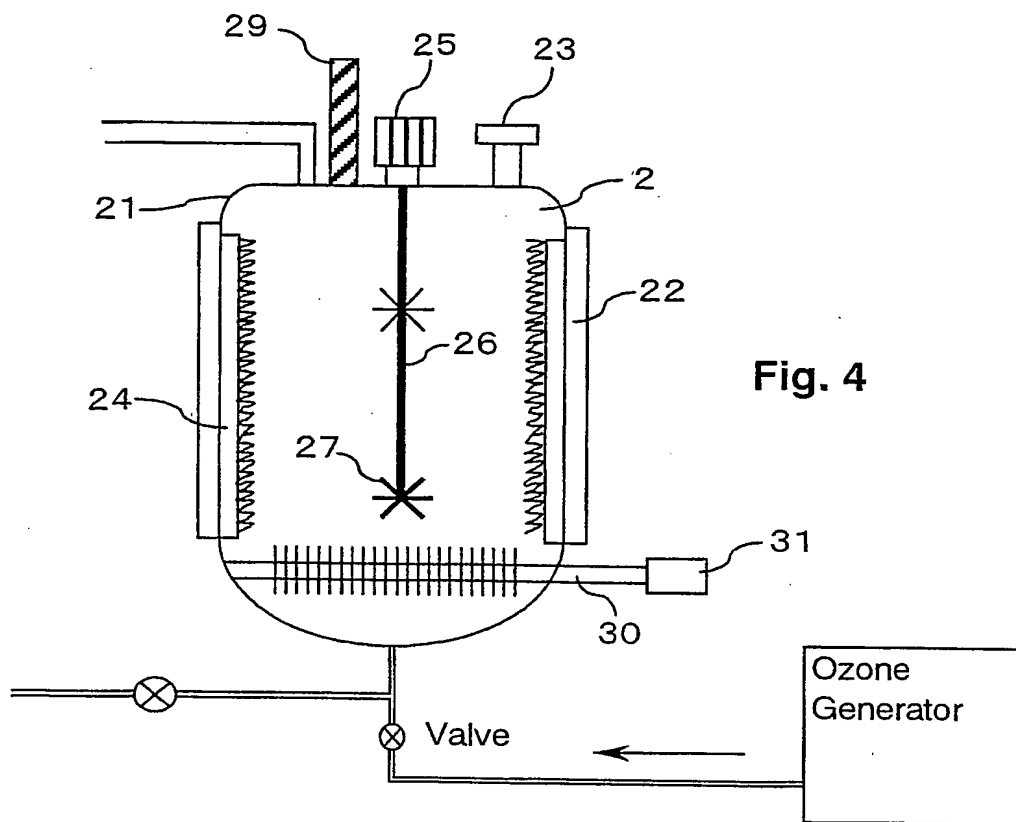
Fig. 1

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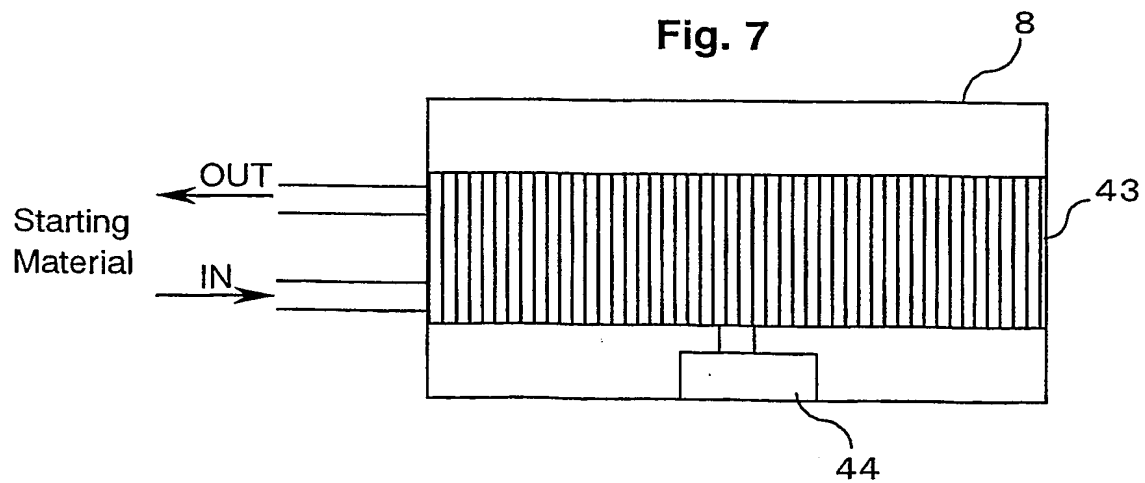
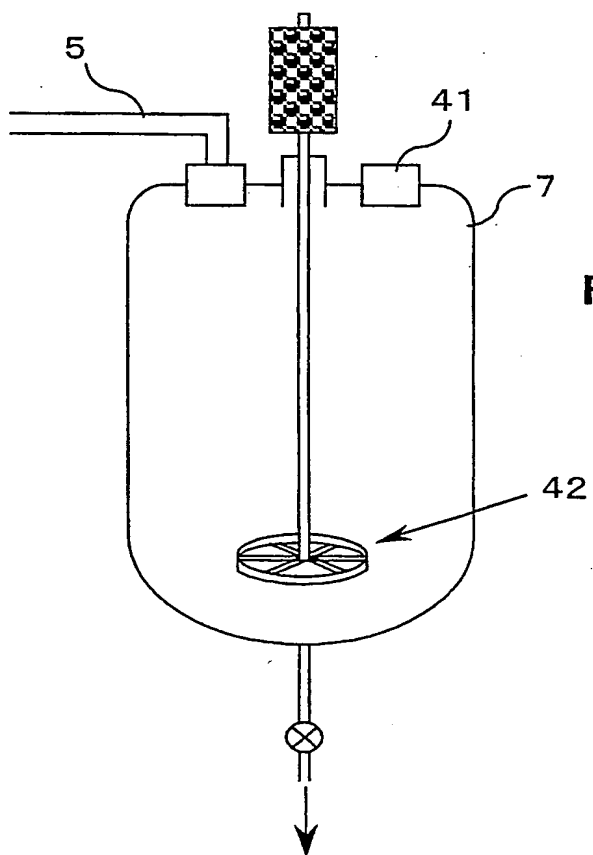


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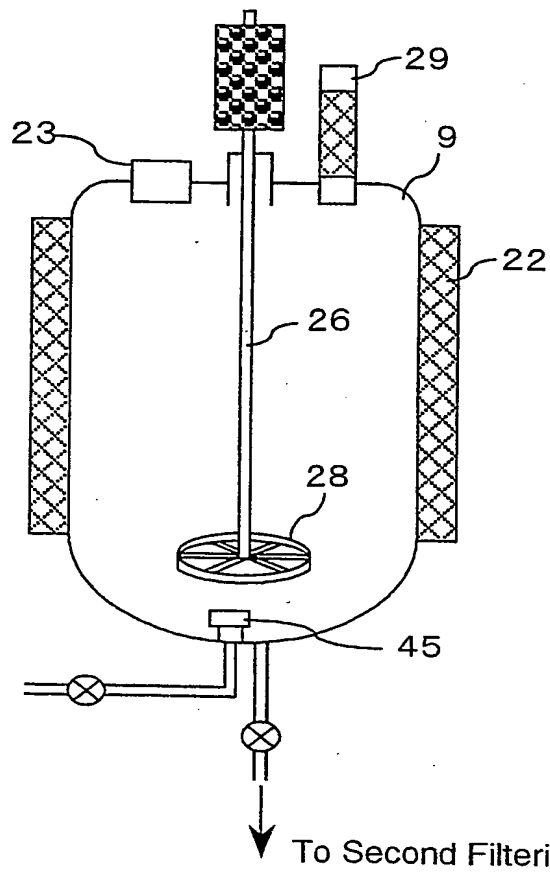


Fig. 8

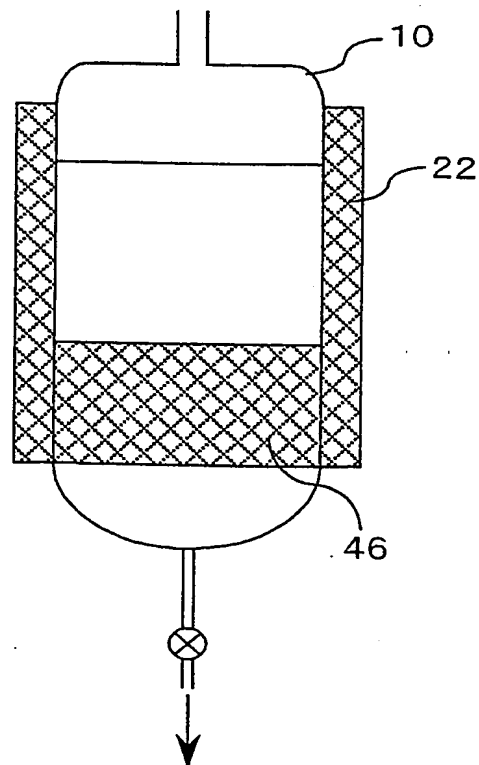
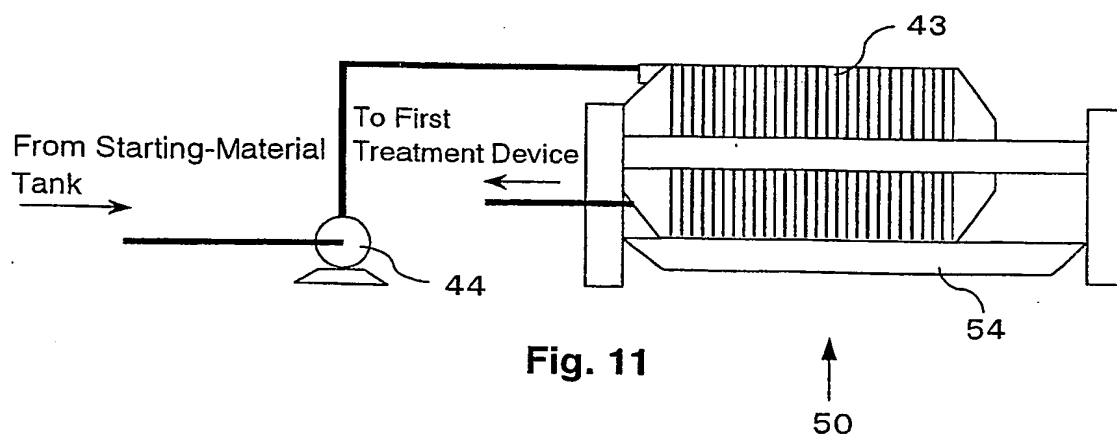
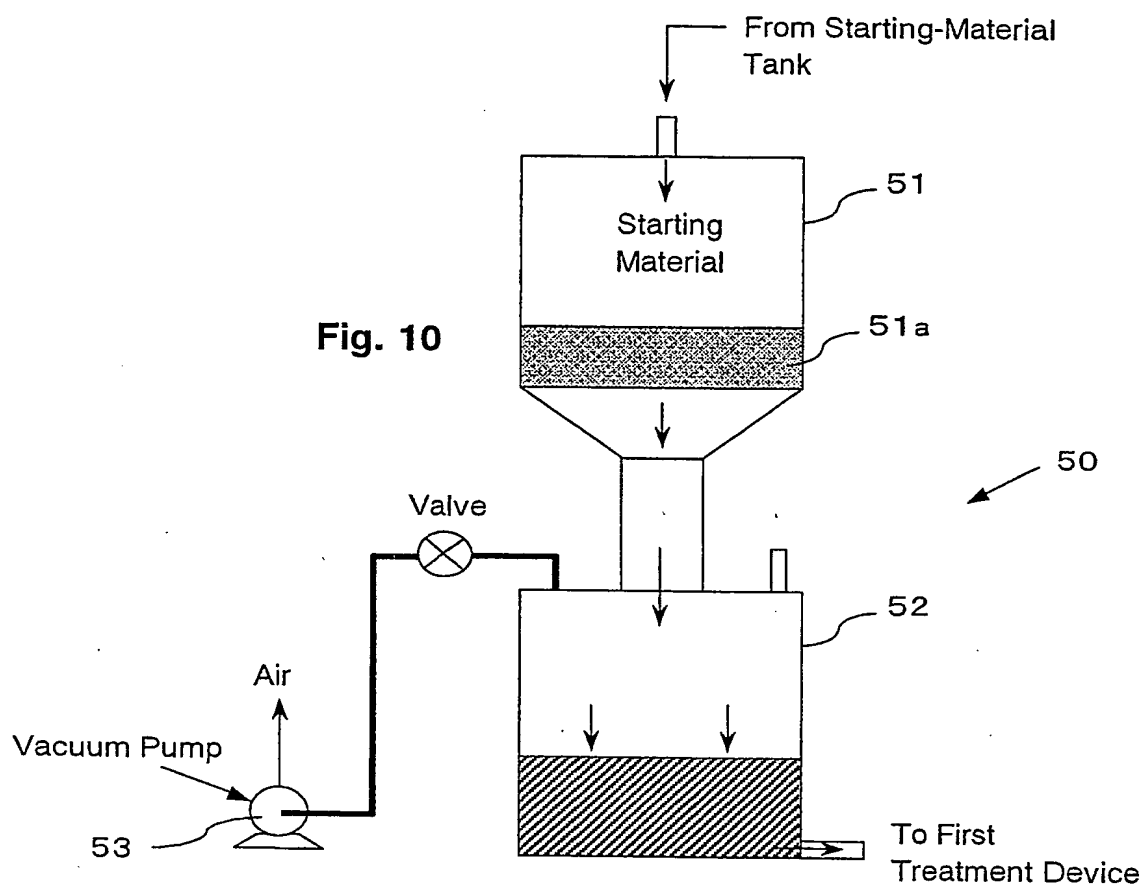
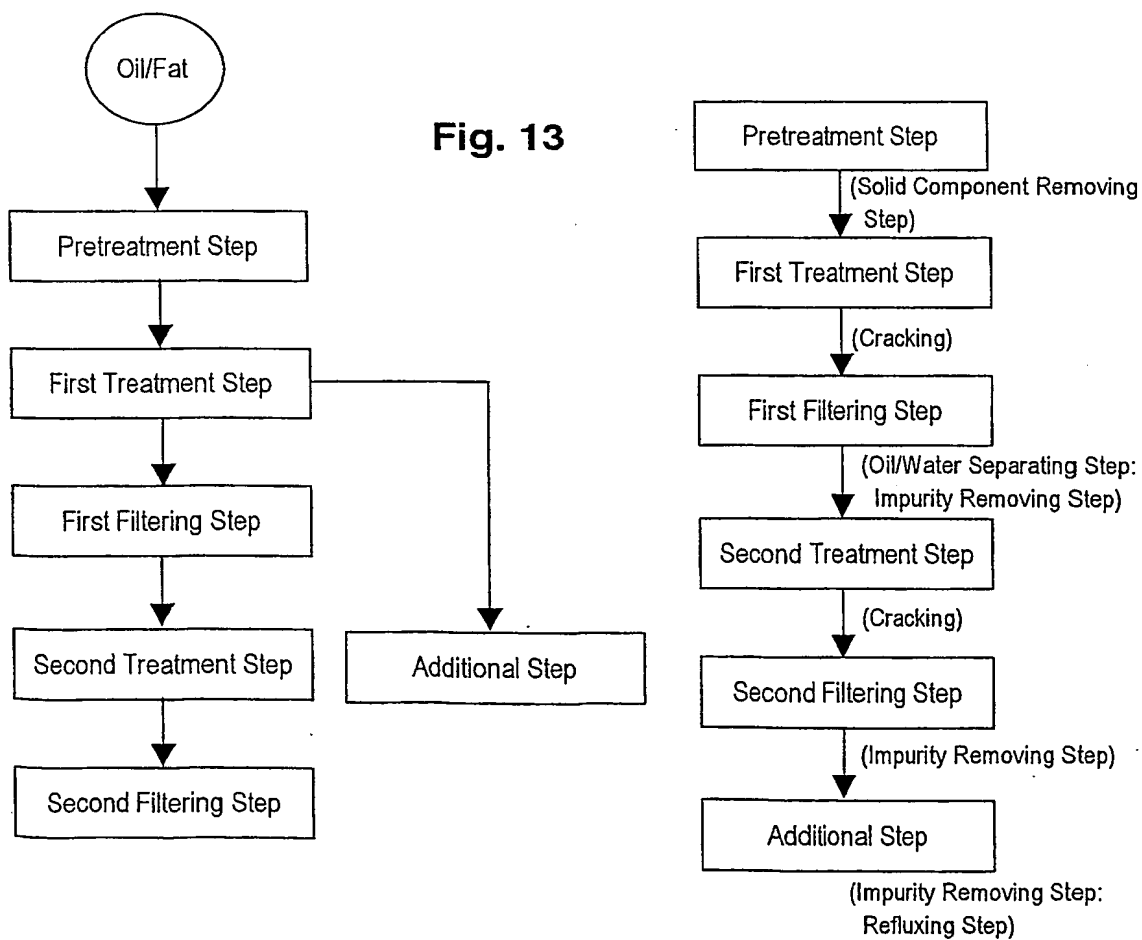
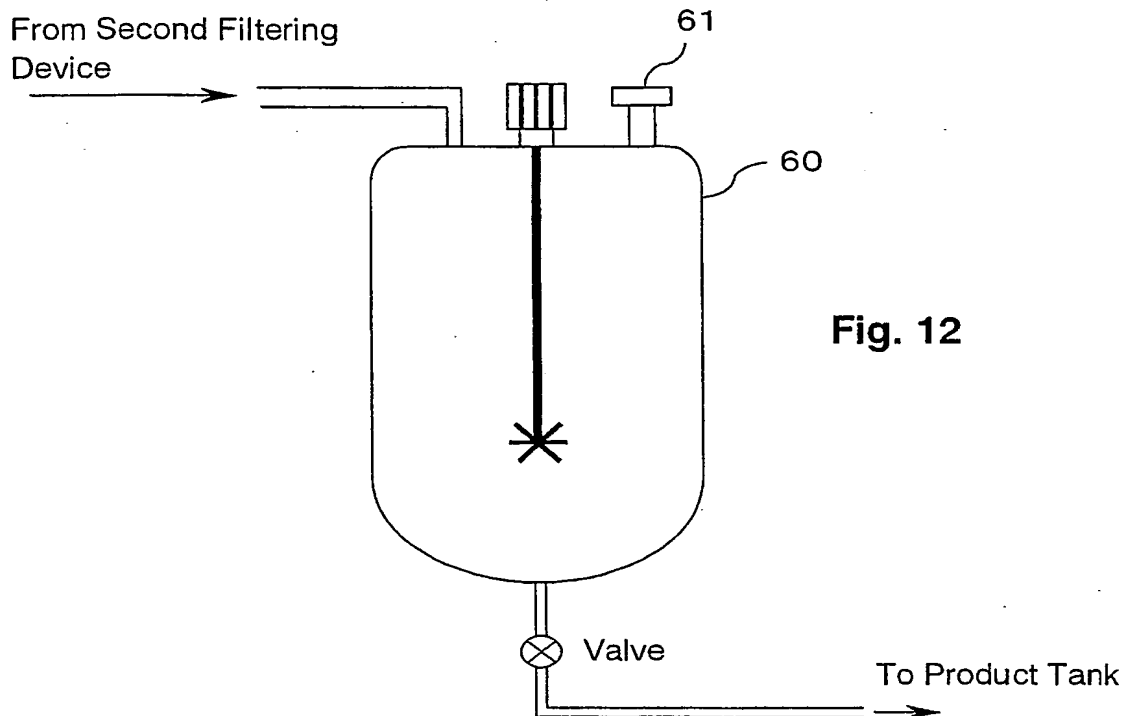


Fig. 9

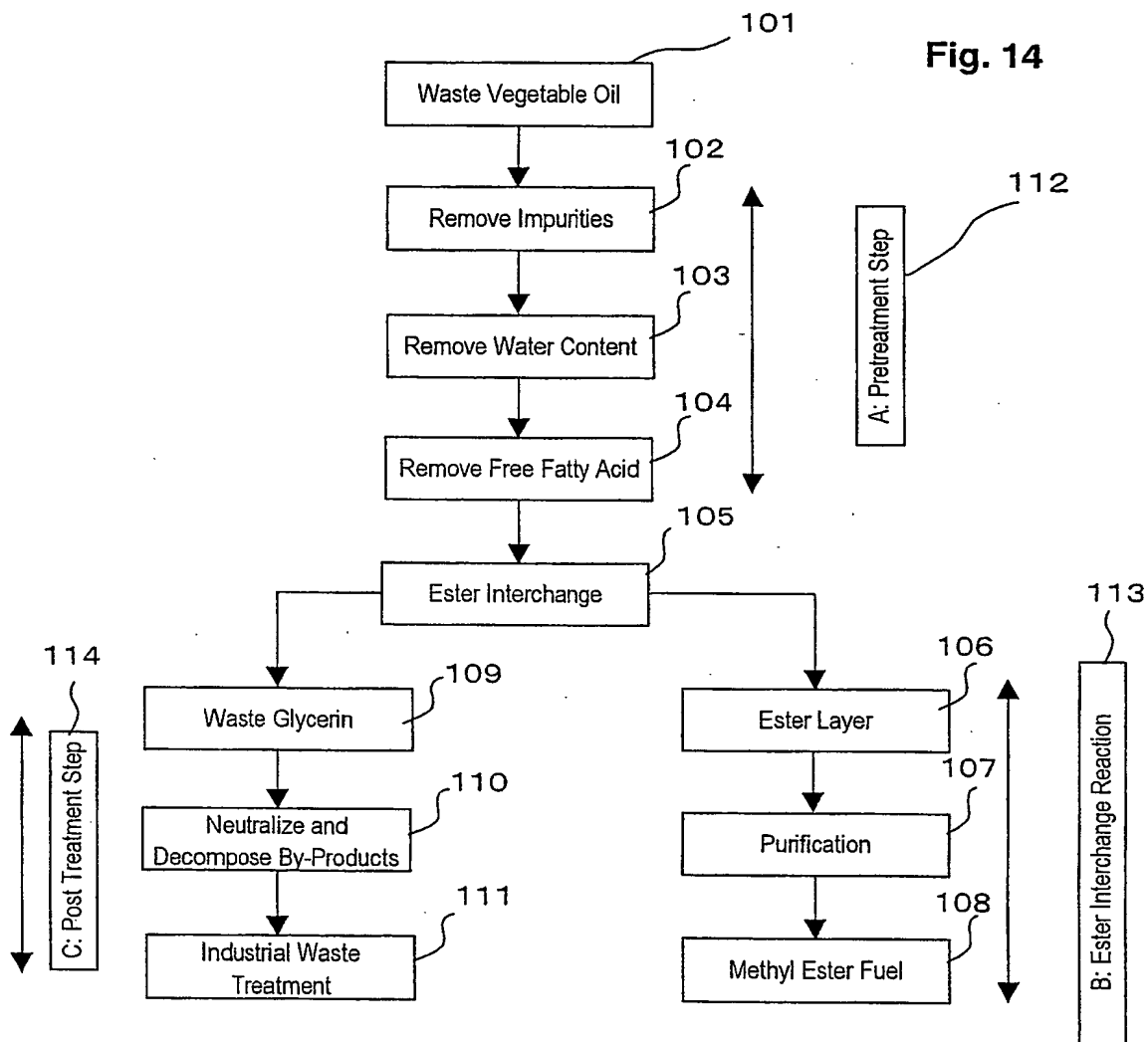
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INTERNATIONAL SEARCH REPORT

International Application No

PCT/02/05682

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C10G55/06 B01J19/18 B01J19/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C10G C10L B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data, COMPENDEX, API Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	paragraphs '0040!-'0058! figures 1,2,6,12; table 1	9-12
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P,X	WO 02 38708 A (MURAKAMI SEISHIRO ;FUJITA HIDEYUKI (JP)) 16 May 2002 (2002-05-16) figures 3,4,6	9-12
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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- *A* document defining the general state of the art which is not considered to be of particular relevance
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Date of the actual completion of the international search

3 April 2003

Date of mailing of the international search report

11/04/2003

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	PATENT ABSTRACTS OF JAPAN vol. 005, no. 045 (C-048), 25 March 1981 (1981-03-25) & JP 55 167249 A (MITSUI PETROCHEM IND LTD), 26 December 1980 (1980-12-26) abstract & DATABASE WPI Section Ch, Week 198110 Derwent Publications Ltd., London, GB; Class E19, AN 1981-16367D XP002237142 & JP 55 167249 A (MITSUI PETROCHEM IND CO LTD), 26 December 1980 (1980-12-26) abstract -----	1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP 02/05682

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 1-8 (part)
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 1-8 (part)

Present claims 1, 7 relate to a process comprising a "first treatment step" and a "second treatment step", which steps comprise the introduction of a compound that is defined by reference to a desirable characteristic or property, namely:

Claim 1: a polymerization inhibitor;

Claim 7: a polymerization inhibitor including a phosphorus compound.

The claims cover all possible compounds having this characteristic or property. However, the application does not provide any further support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT as to the chemical identity of said compounds. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Independent of the above reasoning, the claims also lack clarity (Article 6 PCT), because an attempt is made to define the compound by reference to a result to be achieved. Again, this lack of clarity in the present case is such as to render a meaningful search over the whole of the claimed scope impossible. Consequently, the search has been carried out for those parts of the claims which appear to be clear, supported and disclosed, namely to the claimed process comprising a "first treatment step" and a "second treatment step", which steps may or may not comprise the introduction of a polymerization inhibitor.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/JP02/05682

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
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